Virtual Issue: Designing Polymers for Use in Electrochemical Energy Storage Devices

In this Virtual Issue, we focus on the chemistry of macromolecules needed to advance electrochemical energy storage devices including pseudocapacitors as well as lithium-ion, lithium-metal, magnesium-metal, and redox-flow bat- teries for widespread electrification of transportation and storage on the grid. Success on these fronts hinges on the development of batteries with strict design specifications that carry concomitant demands for the battery's architecture, embodied chemistry, and individual components (i.e., electro- lytes, membranes, electrodes, etc.), which are inextricably coupled in their functions. All must work together to provide long-lasting solutions that can be commercialized and deployed at a cost that disrupts the market, which is currently dominated by the coal, oil, and gas industries.

Batteries in use today are overwhelmingly lead-acid or lithium-ion. The latter owes its recent dominance in the market to portable electronics and the adoption of electric vehicles (EVs) throughout the world and the emergence of high-volume EV battery production facilities (i.e., Giga- factories) that have precipitously dropped the cost of EV batteries. Materials innovations for EV batteries (Figure 1)

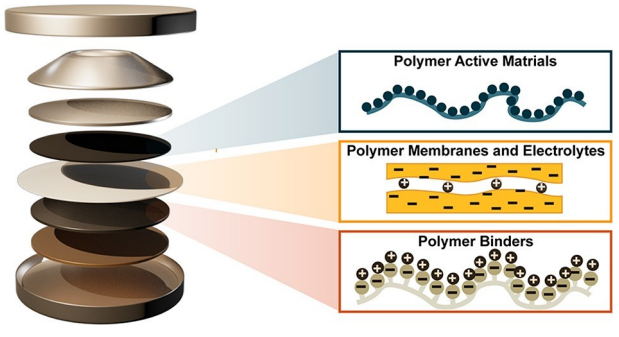

Figure 1. Polymers feature prominently in pseudocapacitors as well as in Li-ion, Li-metal, and Mg-metal batteries: as active materials, electrolytes, membranes, and binders for composite electrodes.

continue to focus on fast-charging cells and on extending vehicle driving range, e.g., through high-voltage cathode and electrolyte development, or by interchanging the graphite anode with lithium metal. Here, the design of polymer and composite electrolytes that prevent dendrite formation remains an area rich with opportunity. In addition, extant safety concerns over EV batteries have elevated solid-state devices to the forefront, where flammable liquid electrolytes are replaced with nonflammable alternatives, including fluoropolymer electrolytes. For emerging markets, such as long-haul trucking and aviation, alternate cathode chemistries will be needed to meet gravimetric energy density requirements, which may be openings for lighter weight (organo)chalcogen-, organic-, and polymer-based electrodes.

For grid modernization, on the other hand, cell chemistries are chosen primarily for their ability to deliver power cost-

effectively on specific time scales: ~seconds for frequency regulation, ~hours for load shifting, and ~days to months for long-duration energy storage. Such systems are also expected to last far longer than EV batteries. For frequency regulation, stationary cells implementing polymer-based electrodes that behave like pseudocapacitors are attractive. For load shifting, redox-flow batteries (RFBs) implementing concentrated solutions of redox-active oligomers and polymers (redoxmers) are potential solutions, provided the flow cells also incorporate ion-selective membranes to prevent redoxmer crossover (Figure 2). Redoxmer-based RFBs are still newcomers to the field, and advances in both redox centers and polymer architectures, as explored in this virtual issue, are still needed for them to prevail over incumbent vanadium RFBs and emerging Na-, K-, and Zn-based cell chemistries.

The prevailing wisdom gleaned from this selection of manuscripts curated over the past 24 months in *Macromolecules* and *ACS Macro Letters* is that macromolecular design brings together leading-edge principles of chemistry, materials, physics, and engineering spanning molecular-to-macroscopic length scales and milliseconds−daylong time scales to prioritize specific classes of polymers for each component of the device. This prioritization is based on a holistic understanding for how structure−transport properties are dictated by the fundamental interactions between polymers, ions, electrons, and other molecules in the device, particularly when the device is driven out of equilibrium during operation. Collectively, these studies have been aided considerably by the consistent use between researchers of model materials classes, whose underlying behaviors have been revealed by harnessing the polymer community's vast synthetic and computational expertise alongside cutting-edge X-ray, neutron, and electron microscopy techniques. We highlight below how the field has begun to converge to key principles influencing decision making in four battery components: polymer electrolytes, polymer separators and membranes, polymer binders, and polymer-based active materials.

Dendrite formation while charging lithium-ion and lithium- metal batteries compromises the safety of EVs, drones, and other applications. As predicted by Monroe and Newman over a decade ago, preventing dendrites from shorting the battery requires high shear-modulus (G) polymer electrolytes, which are often out of reach with typical ion-conducting polymers, such as poly(ethylene oxide) (PEO) or poly(oligo-oxyethylene methacrylate) (POEM), due to their low G relative to lithium metal. To increase G of a soft-ion-conducting polymer, it is common to nanostructure with a hard, glassy matrix, such as polystyrene (PS), by tethering the polymer chain ends to access a variety of multiblock copolymer architectures. This sets up multivariate architecture−transport−mechanical prop- erty relationships that ultimately govern the cell's preferred

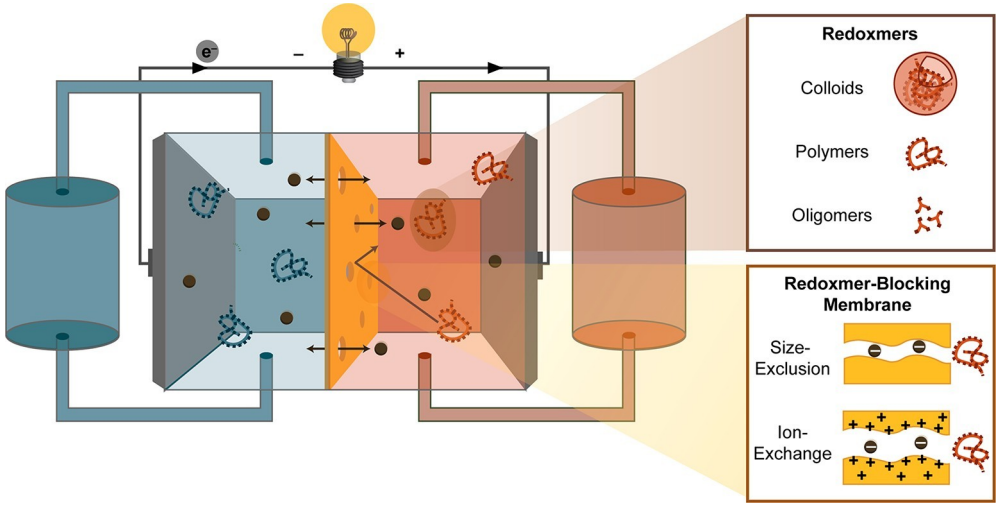

Figure 2. Redox-flow batteries are highly sought after for grid modernization due to their ease of scalability: their design decouples the system's deliverable power, which is tied to the flow cell, from its capacity, which is tied to the redoxmer electrode formulation and the size of the tanks. Redoxmers, consisting of polymer chains modified with redox-active subunits, come in a variety of architectures (e.g., oligomers, polymers, colloids, etc.) that span nano- to macroscopic length scales. The energy efficiency of redoxmer-based flow batteries is influenced by the electrorheological properties of the flowable electrodes as well as the extent to which the redoxmers can be confined to their respective electrode compartments while in the flow cell. Polymer membranes that prevent redoxmer crossover are highly desirable and typically tailored to the redoxmers in place.

temperature range of operation, rate behavior, and the degree to which the intended dendrite-blocking behavior is realized. Balsara and co-workers as well as Epps and co-workers describe such relationships in detail for PS-*b*-PEO and PS-*b*-POEM, respectively, by using electron microscopy, X-ray, and neutron techniques to shed light on the complexity of interactions between lithium salts and BCPs governing microphase segregation, salt-induced crystallization, segmental chain dynamics, and ionic conductivity.[1,2] Interestingly, bulklike ionic conductivity emerges in BCP electrolytes at high MW, without negatively impacting the overall *G*. De Pablo and co- workers as well as Ganesan and co-workers have begun to understand these behaviors by using coarse-grained simu- lations to study the distribution and dynamics of anions and cations, arising from embedded lithium salts, in polymer electrolytes.[3,4] Ganesan, in particular, identifies a Goldilocks principle for polymer electrolytes, where sufficient polarity is needed to reduce ion clustering and increase ionic con- ductivity, where increasing the polarity further tends to slow down segmental chain dynamics to the detriment of ionic conductivity by encouraging stronger polymer−polymer interactions.[4] Experimental insights into both ion and segmental chain dynamics in such systems were reported by Hallinan and co-workers, where structural and stress relaxations in LiTFSI-loaded PS-*b*-PEO were characterized using X-ray photon correlation spectroscopy (XPCS) and rheology and revealed which processes were correlated (or not) on different time scales.[5] These dynamics can be further influenced and potentially controllable by using adaptive polymer networks, as inspired by Segalman and co-workers.[6]

Advancing polymer architectures to access faster ion and segmental chain dynamics has been a major focus, typically involving the incorporation of oligo-ethylene oxides as branches or grafts in the polymer electrolyte. Such designs overcome the notably low ionic conductivity of linear PEO below its melting point, as demonstrated by Lee and co- workers.[7] PEO-nanostructuring as described by Anastasiadis and co-workers using polymer nanoparticles, reminiscent of

Archer and co-workers, likewise appears to provide similar benefits.[8] Instances where those batteries are operated at high current density, where cells tend to polarize, high cation transference number single-ion conductors are desirable. Polyelectrolytes for Li-metal batteries are still nascent in their development and starting to show promise for fast-charge applications as shown by Helms and co-workers.[9] However, as noted by Ganesan, we remain limited in our understanding of the dynamics of ions within polyelectrolytes given their highly polar and strongly interacting character, which are only further obfuscated when the polyelectrolyte is also nanostructured. Early theoretical studies by Lin and co-workers, however, point to an endgame in such cases via inverse phase-segregated morphologies that balance the needs for high ionic conductivity, percolation of ion diffusion pathways, and high G for dendrite blocking.[10] These predictions present exciting new hypotheses for polymer chemists to test experimentally in this vast design space.

The elaboration of polymer electrolytes to dimensionally stable battery components such as separators or membranes has brought new life to the field otherwise captivated by mesoporous polyolefins or perfluorosulfonic acids, which are commercially available. Schaefer and co-workers have reported cross-linked ionomer gels for use as a polysulfide-blocking separator in Mg−S batteries.[11] By controlling cross-linker length, nature of the ionic chemistry, and comonomer ratio, these researchers reduced polysulfide shuttling and MgS formation on the Mg anode. Structure−property relationships linking polymer composition with performance may be used to guide future separators for battery chemistries likewise implementing sulfur cathodes, e.g., Li−S, Na−S, and Zn−S. For RFBs, on the other hand, the membrane is in direct contact with the anolyte and catholyte. One of the outstanding issues in such systems has been related to the extent to which the membrane's transport behavior can be ascribed to a quantitative understanding of the partitioning of ions from the bulk electrolyte into the polymer membrane. To address this issue, Freeman and co-workers used experimental ion sorption,

salt permeability, and ionic conductivity data to develop a general framework for predicting single-ion diffusion coef- ficients in ion-exchange membranes.[12] The results support the hypothesis that condensed counterions in charged, cross-linked membranes migrate along the polymer backbone and contribute to an electrical current in the presence of an externally applied electric field. They also showed that condensed counterions diffuse more rapidly than uncondensed ones because of the shorter distances that condensed counterions need to diffuse to cross the membrane via the polymer backbone.

While polymer electrolytes and membranes primarily derive their characteristics through their interactions with ions (and in some cases, solvent), polymer-based active materials (redoxmers) undergo redox chemistry and therefore carry the burden of managing the transfer and transport of both ions and electrons. In addition, they are expected to maintain their state-of-charge without incurring deleterious side reactions or undergoing significant changes in solvation and, ultimately, solubility. Redoxmers differ from inorganic electrode materials, not only due to their soft nature but also that they do not require ions to intercalate into a rigid solid-state lattice, suggesting that it should possible to design polymers in new ways with functional groups tailored for a specific device's needs for both ionic and electronic conductivity.

In this vein, Scherf, Floudas, and co-workers recently reported a thiophene-based polymer with pendant ionic liquidlike groups.[13] The polymer was designed to separate electronic conductivity along the polythiohene backbone from the ionic conductivity along the imidazolium side chains in a mixed conductor. A detailed study of the nature of the linker group and counterion was performed by examining solid-state structure, conductivity, and thermal properties. This study showed that a low glass temperature, high dielectric constant, smectic layering, and ion-association lengths not exceeding a single layer are required for ion transport; however, the authors point out that improving the electrical conductivity in these mixed conductors should be the focus of further work. Mixed ionic and electronic conductivity in redoxmers was also put to work in condensed-phase redoxmer-based electrodes as reported by Nishide, Oyaizu, and co-workers, who introduced a new class of polyelectrolyte copolymers with TEMPO pendants.[14] Their design featured Bouchet's and Armand's well-known styrenic trifluoromethanesulfonylimide ($TFSI^-$) comonomer to effect Li^+ migration during charge and discharge of the TEMPO units. When the copolymer was used as the cathode in a lithium-ion battery, a high potential (3.7 V) was achieved. Additionally, the self-compensating nature of the comonomer allowed for fast charge−discharge times, ~2 min for each cycle (or 30 C), which can be difficult to achieve even in inorganic intercalation hosts.

Redoxmers with redox-active groups need not only be configured as pendants; redox-active backbones have started to gain attention. One reason for this is that unlike redox-inactive polymers with redox-active pendants, the mass (and volume) of the backbone now favorably contributes to the theoretical capacity of the material. Mecerreyes and co-workers recently studied a series of poly(anthraquinonyl sulfides) with sulfur equivalents, allowing the number of sulfur atoms connecting the anthraquinonyl groups to be systematically varied.[15] Here, both sulfur and anthraquinonyl groups are redox-active such that when used as a cathode in Li-ion batteries, high initial capacity (600 mAh g^{-1}) and good stability were observed; nine

sulfurs per anthraquinone gave the best results. Designing polymers to interface favorably with inorganic active materials has also been useful in the development of binders, e.g., for Si anodes for Li-ion batteries. Taking a cue from Liu and co- workers, published elsewhere, Horie and co-workers studied a cyclopentadithiophene copolymer binder that incorporated oligo-ethylene oxides as Li salt-complexing side chains and terephthalic acid comonomers that adhere to Si, which undergoes >300% volume changes during electrochemical cycling.[16] Impressive initial capacities of ~2500 mAh g^{-1} were reported for cells incorporating these volume change-compensating composite anodes.

Redoxmer-based composite electrodes are also filling gaps in technology where fast charge or discharge is needed: for example, for acceleration or regenerative breaking in EVs or for frequency regulation in the grid. Such designs often suffer from a trade-off in that fast charge or discharge is concomitant with lower capacity, since most of these devices use high-surface- area carbon where charge is stored electrostatically at the surface. Pseudocapacitive electrodes that combine surface- charging effects with formal Faradaic processes may become increasingly important for these applications. In this regard, polymers cannot be overlooked. Stuparu, Madhavi, and co- workers developed pendant polymers using a Buckybowl motif, which were prepared by a ring-opening method using a Grubbs second-generation catalyst.[17] The polymers exhibited pseudo-capacitive behavior and impressive stability after 10000 cycles. Similarly effective, He, Meng, and co-workers designed pseudocapacitive polymers with redox-active groups directly in the polymer backbone.[18] Interestingly, these researchers used building blocks, designed to be insoluble or soluble, and varied each monomer's incorporation in the polymers to optimize film-forming ability without perturbing the redox- active main chain.

Understanding how polymer design rules differ for redoxmer electrodes in the condensed phase and soluble redoxmers for RFBs is an ongoing area of importance. Redoxmers experience state-of-charge dependent backbone−pendant group, polymer−electrolyte, and polymer−polymer interactions that dictate the electroreversibility and rheological characteristics of the flowable electrode. These influence mass transfer and pumping losses and place limits on the flowable electrode's volumetric capacity. As shown in a report by Rodríguez-López, Moore, and co-workers, for redox-active cyclopropenium cations incorporated in polystyrenes with different pendant designs, longer spacers are needed to ensure electroreversi- bility.[19] Despite their highly charged nature, the redoxmers were soluble and suitable for testing in RFBs that incorporated redoxmer-blocking membranes, such as those based on polymers of intrinsic microporosity (PIMs), which had been reported previously. Some loss in capacity was observed during repeated cycling, but the strategy of chemically isolating the pendant redox group from a potentially reactive polymer backbone is a critical concern for redoxmer development generally, as RFBs for the grid should last >10000 cycles, and will depend strongly on the exact identity of both.

We hope that with this virtual issue we inspire, by example, the next generation of both concepts, materials, and teams of researchers in this exciting area for polymer science. It is noteworthy that many of these recent studies involve deep collaborations that span disciplines, rather than the conven- tional trifecta of synthesis, theory, and characterization within the same discipline. To close, we offer further where the field

might go in the next several years to address outstanding questions about the fundamentals of polymer behavior in electrochemical energy storage devices as well as emerging technology needs (Figure 3).

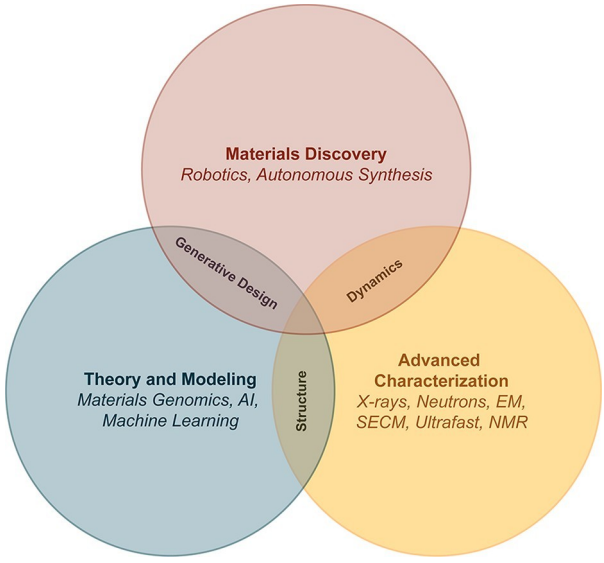

Figure 3. Emerging opportunities in at the intersection of materials discovery, theory, and modeling have the potential to direct the field toward the generative design of polymer-based materials for electrochemical energy storage devices. In particular, robotics for high-throughput synthesis, fabrication, and screening capabilities have advanced considerably in the past 5 years, making it possible for such data sets to serve as inputs for AI and machine learning to understand the logic behind macromolecular design for specific property sets. Library design can be informed *a priori* by high-throughput DFT- based screens. To arrive at a deeper understanding of fundamental architecture−transport relationships in polymer electrolytes, membranes, and redoxmers, the field should increasingly make use of advanced characterization techniques, where dynamic information across time scales is possible. Similarly, data interpretation to arrive at structural details for how polymers interact with ions and solvent (or with each other) necessitates the use of computational resources, tailored algorithms, and new physical models for the observed behavior under device-relevant conditions.

In electrochemical energy storage devices, energy should convert to useful work with minimal loss. Components in such devices, therefore, need to contribute favorably to energy conversion. As such, the embodied macromolecules in those components should be tailored for efficient transport of ion, electrons, and mass to avoid unnecessary energy losses, which manifest as overpotentials. Perhaps too often we have evaluated the model classes of materials (e.g., ethylene oxides, styrenics, and styrenic TFSIs) as polymer electrolytes, polymer binders, polymer membranes, or redoxmers without consider- ing that each may have a different set of requirements that must be met to minimize energy losses in the device as a whole. Therefore, we strongly encourage the community to think beyond convention and beyond today's model materials classes, particularly as it has become necessary to overcome their inherent transport bottlenecks and stability issues. This will be particularly useful for the discovery of stable redoxmers, polyelectrolytes as low-loss ionic materials, and structurally rigid polymers that uncouple various transport processes from polymer segmental chain dynamics. We also encourage the

community to develop, more broadly, polymers with an expanded set of architectural attributes. For example, branched polymer architectures (e.g., dendrimers or hyberbranched polymers) could provide advantages over linear architectures with respect to rheology at different states of charge in RFBs to reduce pumping losses. Furthermore, polymer architectures need not be statically configured in the device. The abundance of volume changes in metal anodes as well as in conversion or alloying electrodes requires compliant binders and electrolytes (for solid-state cells), which might favor reconfigurable polymers. Supramolecular motifs integrated within the polymer's larger architectural framework may provide powerful solutions to such problems, as might dynamic covalent motifs (e.g., vitrimers). We note that responsive polymers can be engineered to evolve their form or function according to thermal or chemical gradients, which opens doors for sustained development of components with adaptive or regenerative behaviors not available with present-day chemistries.

We anticipate that the design of new polymers with a specific property sets (e.g., ion-pairing strength, electrolyte swelling, redox potential, chemical stability, etc.) will be aided significantly by deep computational insights. Such insights can be made *a priori* using high-throughput density functional theory-based (DFT) methods, such as the Materials Project. Alternatively, the collective discoveries of our community over the past decades can serve as an initial source of information for algorithm-driven artificial intelligence (AI) and machine learning (ML). We further see advances in robotics and flow chemistry for high-throughput synthesis, tied to ML and AI, as well as autonomous synthesis such as Cronin's Chemputer as an invigorating and relentless means to drive new discoveries that contribute to the body of knowledge of our field but has the potential to be unbiased yet purposeful.

While the intersection of polymer synthesis and computa- tional prowess is imminent and compelling, so will be the validation of our physical models for polymer behavior using advanced neutron techniques (e.g., spin echo), coherent X-rays (e.g., XPCS), and electron microscopy (e.g., cryo-EM and direct electron detectors). There may further be opportunities in the chemical specificity of ultrafast X-ray and 2-D IR or Raman spectroscopic methods, *in situ* multinuclear NMR spectroscopy, and near-field spectromicroscopy, where the bounds of spatiotemporal resolution are pushed to understand the chemical evolution of materials in and out of equilibrium as ions and mass redistribute in various components, or across interfaces between electrodes and electrolytes, according to local chemical potential gradients. Presently, we have only bulk and indirect means of characterizing such processes, which limits our understanding of how local energy landscapes for ion and mass transport evolve in time during the device's operation to give rise to the observed macroscopic cell behavior.

It is also clear that we need to think about the ions of the future: batteries that incorporate earth-abundant ions like Na, K, Mg, Al, and Zn are increasingly attractive for battery technologies at scale. The foundations by which these ions interact with polymers have not yet been elucidated in sufficient detail, and design rules known for lithium ions do not universally apply to other ions. Again, new polymers with respect to both composition and architecture may be required to meet the demands for power, cycle-life, cost, etc., for the devices that integrate them.

Finally, we would like to point out the enormous opportunity to train the next generation of scientists and

engineers in this burgeoning area of cross-disciplinary research. Electrochemistry is one of the most mature subdisciplines of chemistry. Its theories are robust and have withstood the test of time. Its importance in catalysis, energy science, and so forth cannot be understated. It is disappointing how few research- intensive institutions offer a graduate curriculum in electro- chemistry. We hope that this will change. A firm grasp of electrochemistry and transport physics is the only way to advance the field's cutting edge. Moreover, it seems appropriate to consider new ways of merging polymer science, engineering, and electrochemistry in modern curricula. Certainly, students trained in these areas will be highly sought after in the private, government, and policy sectors; as entrepreneurs and champions for new technology; and they will be well-positioned to launch creative new research programs as independent investigators.

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Notes

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

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REFERENCES

(1) Thelen, J. L.; Wang, A. A.; Chen, X. C.; Jiang, X.; Schaible, E.; Balsara, N. P. Correlations between Salt-Induced Crystallization, Morphology, Segmental Dynamics, and Conductivity in Amorphous Block Copolymer Electrolytes. *Macromolecules* 2018, *51*, 1733−1740.

(2) Gartner, T. E., III; Morris, M. A.; Shelton, C. K.; Dura, J. A.; Epps, T. H., III Quantifying Lithium Salt and Polymer Density Distributions in Nanostructured Ion-Conducting Block Polymers. *Macromolecules* 2018, *51*, 1917−1926.

(3) Chu, W.; Qin, J.; de Pablo, J. J. Ion Distribution in Microphase-Separated Copolymers with Periodic Dielectric Permittivity. *Macro- molecules* 2018, *51*, 1986−1991.

(4) Wheatle, B. K.; Lynd, N. A.; Ganesan, V. Effect of Polymer Polarity on Ion Transport: A Competition between Ion Aggregation and Polymer Segmental Dynamics. *ACS Macro Lett.* 2018, *7*, 1149− 1154.

(5) Oparaji, O.; Narayanan, S.; Sandy, A.; Ramakrishnan, S.; Hallinan, D., Jr. Structural Dynamics of Strongly Segregated Block Copolymer Electrolytes. *Macromolecules* 2018, *51*, 2591−2603.

(6) Sanoja, G. E.; Schauser, N. S.; Bartels, J. M.; Evans, C. M.; Helgeson, M. E.; Seshadri, R.; Segalman, R. A. Ion Transport in Dynamic Polymer Networks Based on Metal−Ligand Coordination: Effect of Cross-Linker Concentration. *Macromolecules* 2018, *51*, 2017−2026.

(7) Kim, B.; Chae, C.-G.; Satoh, Y.; Isono, T.; Ahn, M.-K.; Min, C.- M.; Hong, J.-H.; Ramirez, C. F.; Satoh, T.; Lee, J.-S. Synthesis of Hard−Soft−Hard Triblock Copolymers, Poly(2-naphthyl glycidyl ether)-*block*-poly[2-(2-(2-methoxyethoxy)ethoxy)ethyl glycidyl ether]-*block*-poly(2-naphthyl glycidyl ether), for Solid Electrolytes. *Macromolecules* 2018, *51*, 2293−2301.

(8) Glynos, E.; Petropoulou, P.; Mygiakis, E.; Nega, A. D.; Pan, W.; Papoutsakis, L.; Giannelis, E. P.; Sakellariou, G.; Anastasiadis, S. H. Leveraging Molecular Architecture To Design New, All-Polymer Solid Electrolytes with Simultaneous Enhancement in Modulus and Ionic Conductivity. *Macromolecules* 2018, *51*, 2542−2550.

(9) Li, L.; Ma, L.; Helms, B. A. Architected Macroporous Polyelectrolytes That Suppress Dendrite Formation during High- Rate Lithium Metal Electrodeposition. *Macromolecules* 2018, *51*, 7666−7671.

(10) Zhai, C.; Zhou, H.; Gao, T.; Zhao, L.; Lin, S. Electrostatically Tuned Microdomain Morphology and Phase-Dependent Ion Trans- port Anisotropy in Single-Ion Conducting Block Copolyelectrolytes. *Macromolecules* 2018, *51*, 4471−4483.

(11) Ford, H. O.; Merrill, L. C.; He, P.; Upadhyay, S. P.; Schaefer, J. L. Cross-Linked Ionomer Gel Separators for Polysulfide Shuttle Mitigation in Magnesium−Sulfur Batteries: Elucidation of Structure− Property Relationships. *Macromolecules* 2018, *51*, 8629−8636.

(12) Kamcev, J.; Paul, D. R.; Manning, G. S.; Freeman, B. D. Ion Diffusion Coefficients in Ion Exchange Membranes: Significance of Counterion Condensation. *Macromolecules* 2018, *51*, 5519−5529.

(13) Pipertzis, A.; Mühlinghaus, M.; Mezger, M.; Scherf, U.; Floudas, G. Polymerized Ionic Liquids with Polythiophene Back- bones: Self-Assembly, Thermal Properties, and Ion Conduction. *Macromolecules* 2018, *51*, 6440−6450.

(14) Tokue, H.; Murata, T.; Agatsuma, H.; Nishide, H.; Oyaizu, K. Charge−Discharge with Rocking-Chair-Type Li+ Migration Charac- teristics in a Zwitterionic Radical Copolymer Composed of TEMPO and Trifluoromethanesulfonylimide with Carbonate Electrolytes for a High-Rate Li-Ion Battery. *Macromolecules* 2017, *50*, 1950−1958.

(15) Gomez, I.; Leonet, O.; Blazquez, J. A.; Grande, H.-J.; Mecerreyes, D. Poly(anthraquinonyl sulfides): High Capacity Redox Polymers for Energy Storage. *ACS Macro Lett.* 2018, *7*, 419−424.

(16) Yao, C.-F.; Wang, K.-L.; Huang, H.-K.; Lin, Y.-J.; Lee, Y.-Y.; Yu, C.-W.; Tsai, C.-J.; Horie, M. Cyclopentadithiophene−Terephthalic Acid Copolymers: Synthesis via Direct Arylation and Saponification and Applications in Si-Based Lithium-Ion Batteries. *Macromolecules* 2017, *50*, 6924−6934.

(17) Mishra, A.; Ulaganathan, M.; Edison, E.; Borah, P.; Mishra, A.; Sreejith, S.; Madhavi, S.; Stuparu, M. C. Polymeric Nanomaterials Based on the Buckybowl Motif: Synthesis through Ring-Opening Metathesis Polymerization and Energy Storage Applications. *ACS Macro Lett.* 2017, *6*, 1212−1216.

(18) Wang, Y.; Li, W.; Guo, Y.; Cao, J.; Murtaza, I.; Shuja, A.; He, Y.; Meng, H. Recombination Strategy for Processable Ambipolar Electroactive Polymers in Pseudocapacitors. *Macromolecules* 2018, *51*, 7350−7359.

(19) Montoto, E. C.; Cao, Y.; Hernańdez-Burgos, K.; Sevov, C. S.; Braten, M. N.; Helms, B. A.; Moore, J. S.; Rodríguez-Lopéz, J. Effect of the Backbone Tether on the Electrochemical Properties of Soluble Cyclopropenium Redox-Active Polymers. *Macromolecules* 2018, *51*, 3539−3546.